Supporting Information for:

Bulk growth, structure, and characterization of the new monoclinic $TbCa_4O(BO_3)_3$ Crystal

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Contents:

(1) The details of the thermal expansion experiment:

The thermal expansion experiments of $TbCa_4O(BO_3)_3$ were carried out using a thermal dilatometer (Diamond TMA) over the temperature range of 30-300 ℃ at a rate of 5 ℃/min. For the monoclinic TbCOB crystal with space group Cm, the thermal expansion coefficient with respect to the crystallographic axis a, b and c was calculated, respectively. The average linear thermal expansion can be obtained according to the following formula:

$$\alpha(T_0 \rightarrow T) = \frac{\Delta L}{L_0} * \frac{1}{\Delta T}$$

where $\alpha(T_0 \rightarrow T)$ is the average linear thermal expansion coefficient over the temperature range from T_0 to T, L_0 is the sample length at T_0, ΔL is the length changed when the temperature changes from T_0 to T, and $\Delta T = T - T_0$ is the temperature change. The values of the average linear thermal expansion coefficients of TbCOB crystal for the

temperature range of 30 to 300 ℃ were α_a= 8.82 × 10^{-6} K^{-1}, α_b= 4.33 × 10^{-6} K^{-1} and α_c= 9.84 × 10^{-6} K^{-1}, respectively.

(2) Figures and Tables:

Table S1. Selected crystal data and structure refinement parameters for $TbCa_4O(BO_3)_3$.

Table S2. Refined atomic coordinates and isotropic displacement parameters for $TbCa_4O(BO_3)_3$.

Figure S1. The obtained TbCOB crystal with white inclusions during the shoulder process.

Figure S2. Room temperature absorption spectrum of TbCOB single crystal.

Table S1. Selected crystal data and structure refinement parameters for $TbCa_4O(BO_3)_3$.

Empirical formula	$Tb_{0.99}Ca_{4.01}B_3O_{10}$
Formula weight	509.89
Temperature	293(2) K
Radiation, wavelength	Mo-Kα, 0.71073 Å
Crystal system	monoclinic
Space group	*Cm* (No.8)
Unit cell dimensions	a = 8.0715(7) Å
	b = 16.0000(15) Å
	c = 3.5454(3) Å
β	101.2550(10)°
Unit Cell volume, Z	449.06(7) Å^3, 2
Density (*calc.*)	3.771 g/cm^3
Absorption coefficient	10.094 cm^{-1}
Theta range for data collection/ deg.	2.55 to 27.44
F(000)	479
Limiting indices	-9⩽h⩽10, -20⩽k⩽20, -4⩽l⩽1
Reflections collected/ unique	1421/718
R(int)	0.0197
Flack parameter	0.50(3)
Data/ restraints/ parameters	718/2/83
Goodness-of-fit on F^2	1.468
Final R indices [a] [$I>2\sigma_{(I)}$]	R_1 = 0.0305
	wR_2 = 0.0838
Final R indices [a] [all data]	R_1 = 0.0327
	wR_2 = 0.0792

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, and $w = 1/[\sigma^2F_o^2 + (A\cdot P)^2 + B\cdot P]$, $P = (F_o^2 + 2F_c^2)/3$; A and B are weight coefficients.

Table S2. Refined atomic coordinates and isotropic displacement parameters for $TbCa_4O(BO_3)_3$.

Atoms	Wyckoff	*x*	*y*	*z*	U_{eq} (Å^2)	*Occupancy*
Tb1/Ca1	*2 a*	0.00003(7)	0	00041(7)	0.0071(3)	0.96(2)/ 0.04(2)
Tb2/Ca2	*4 b*	0.1400(3)	0.38742(13)	0.3192(6)	0.0086(10)	0.043(7)/ 0.957(7)
Ca3	*4 b*	0.2589(3)	0.18157(16)	0.6424(7)	0.0096(9)	1.0
B1	*2a*	0.373(3)	0	0.684(6)	0.008(4)	1.0
B2	*4b*	0.9486(19)	0.1945(10)	0.065(5)	0.011(3)	1.0
O1	*2a*	0.821(2)	0	0.409(5)	0.009(4)	1.0
O2	*4b*	0.4579(11)	-0.0736(5)	0.735(3)	0.010(2)	1.0
O3	*2a*	0.192(2)	0	0.594(6)	0.014(4)	1.0
O4	*4b*	0.0818(11)	0.1426(6)	0.064(3)	0.010(2)	1.0
O5	*4b*	0.9665(13)	0.2688(6)	0.263(3)	0.014(2)	1.0
O6	*4b*	0.7876(12)	0.1718(6)	-0.130(3)	0.013(2)	1.0

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor

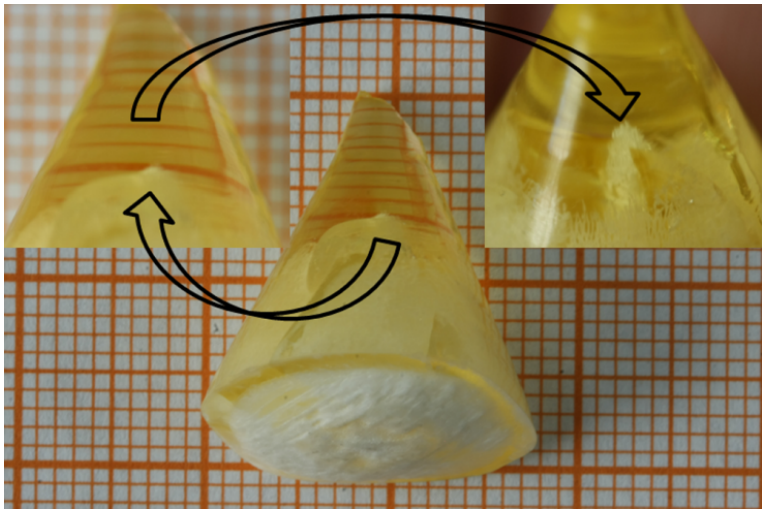

Figure S1. The obtained TbCOB crystal with white inclusions during the shoulder process.

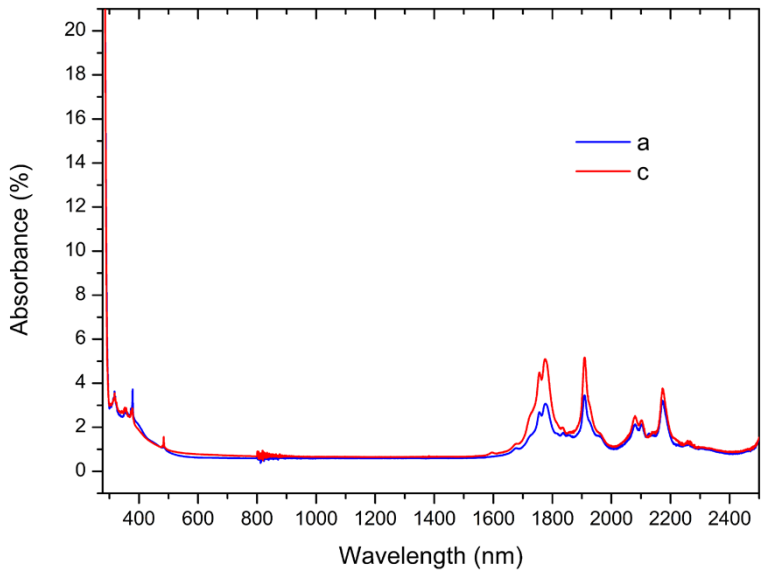

Figure S2. Room temperature absorption spectrum of TbCOB single crystal.